I had rather raise up one man to front the world than half a hundred dependents that dare not breathe the outside air.

Louis J. Halle, Jr.

Spring in Washington, 1947

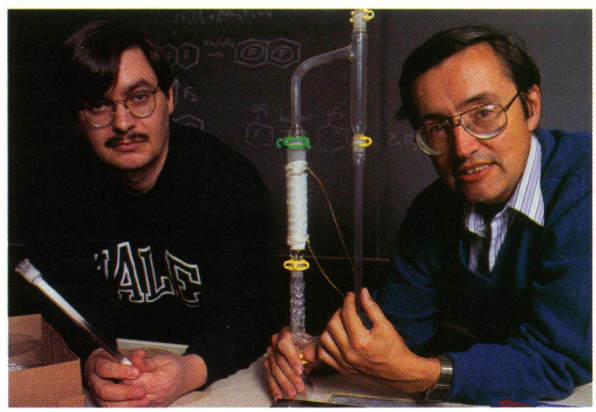
Forum

Turning CFCs into Salt

Following a widespread ban on the production of ozone-destroying chlorofluorocarbons (CFCs), researchers are scrambling to turn massive stockpiles of the substances into useful or at least benign materials. In one example at Yale University, scientists are converting CFCs into table salt and other harmless solids using a chemical found in rhubarb leaves.

Professor Robert H. Crabtree and graduate student Juan Burdeniuc say they've developed an inexpensive system for destroying CFC stockpiles—including an estimated 100 million pounds of Freon, a coolant used in refrigerators and car air conditioners. By passing vaporized CFCs through a packed bed of powdered sodium oxalate at about 550°F, Crabtree reported in the 19 January 1996 issue of *Science*, it's easy to generate carbon, salt, and sodium fluoride, a toothpaste ingredient. "The apparatus is remarkably simple," he says. "It's a so-called 'hot tube' arrangement."

R. Tom Baker, a project leader and research associate for the DuPont Company of Wilmington, Delaware, once the world's largest CFC maker, says it remains to be seen whether Crabtree's technique will be cost-effective, in part because it generates salt, a low-cost commodity that poses handling and disposal problems. But, Baker adds, Crabtree's process is "intriguing" because at lower temperatures, it reportedly converts CFCs into valuable fluorocompounds—a category that includes mefloquine (an antimalarial drug), ciprofloxacin (an antibiotic), halothane (an anesthetic), and surface coatings such as Teflon.

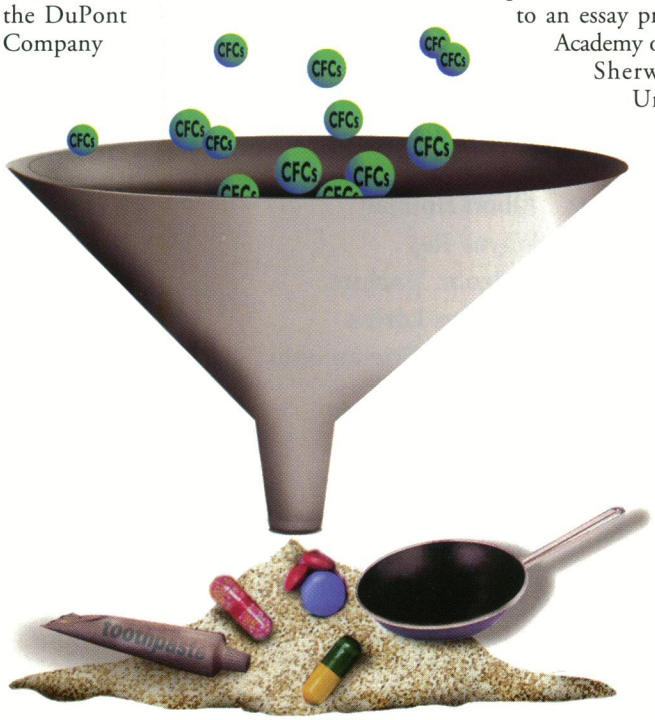


Yale University

Conversion collaboration. Juan Burdeniuc (left) and Robert H. Crabtree (right) have developed a "hot tube" to turn CFCs into salt.

Chlorine atoms from CFCs destroy stratospheric ozone, exposing people, plants, and animals to harmful UV radiation, which is linked to skin cancer, cataracts, crop damage, and global climate changes.

At altitudes above 18 miles, sunlight strips chlorine atoms from CFCs, according to an essay prepared for the National Academy of Sciences by Professor F. Sherwood Rowland of the University of California–Irvine. Chlorine atoms react with ozone to form chlorine oxide, a free radical, which sets off an ozone-destroying chain reaction, writes Rowland, co-recipient of the 1995 Nobel Prize in chemistry for ozone research. Because a lone chlorine atom can destroy 100,000 ozone molecules, CFCs annually deplete ozone levels in an area the size of Europe in the earth's gaseous shield above Antartica. People in the Northern Hemi-sphere receive an annual dose of UV radiation that's 5% more potent than it was in the 1980s, Rowland reports, and skin cancer rates are now 10 times higher than in the 1950s. Though scientists haven't found a biological link between ozone loss and cancer, he says, epidemiological evidence is mounting.



Recycled CFCs. New processes turn ozone-destroying chlorofluorocarbons into sodium oxalate used in products such as salt, sodium fluoride, drugs, and surface coatings for cookware.

Consequently, CFC production was banned in most developed countries beginning in 1996 as part of the international Montreal Protocol. But existing CFC supplies can still be used in older-model cars and refrigeration equipment, explains Sue Stendebach, an acting branch chief in the Stratospheric Protection Division at the EPA. In the future, Stendebach says, the EPA might work to have congress amend the Clean Air Act to require the destruction of CFC stockpiles, "but only when demand starts going down significantly."

Crabtree's invention is one of a dozen CFC conversion technologies now under development, Stendebach says. Two U.S. firms, Commodore CFC Technologies, Inc. of Columbus, Ohio, and Process Technologies, Inc. (PTI) of Boise, Idaho, are getting into the business in a big way.

Like Crabtree's process, the Commodore and PTI techniques generate salts. Using ammonia, Commodore solvates calcium, sodium, and other metals to produce a solution rich in free electrons, which transforms CFCs into salts. The closed system doesn't require heat, and it doesn't pollute the air, Commodore president Jim DeAngelis says.

The PTI system sends gas-phase CFCs through an aluminum box lined with lamps containing mercury, which vaporizes

and emits UV light, explains Michael S. Swan, PTI's vice president for business development. Just as sunlight splinters CFCs, the UV lamps release highly reactive molecules known as free radicals. To prevent these promiscuous molecules from bonding with unsuitable partners, Swan says, PTI "mates" them with a solid reagent containing calcium oxide, thereby producing salts such as calcium chloride.

DuPont, meanwhile, is focusing on techniques to convert CFCs into less destructive hydrochlorofluorocarbons (HCFCs), as well as chlorine-free hydrofluorocarbons (HFCs), which may not destroy ozone but may contribute to the greenhouse effect. Baker has patented a process that turns CFC-113a into HCFC-123 using homogeneous catalysis (in which the catalyst and the reactants are in the same phase) without generating salts. When gas-phase CFCs and hydrogen are fed into a reactor, he explains, chlorine atoms are simply replaced by hydrogen. Compared to more traditional heterogeneous catalysis, the homogeneous system is less likely to generate undesirable byproducts, Baker says, and it isn't deactivated by heat.

To be cost-effective, Swan says, CFC conversion technologies must compete with incineration, which can cost up to $15 per pound. Swan claims he can destroy CFCs for $2–$4 per pound. DeAngelis says his system is 30–50% cheaper than incineration. Key Commodore ingredients—sodium and calcium—cost between $2.25 and $2.45 per pound, DeAngelis says. By comparison, laboratory samples of the sodium oxalate used in Crabtree's process may be priced at $40 per pound. But Gregory E. Gardiner, Yale's director of cooperative research, says larger quantities are available for $2.25 per pound.

Cytokine Knockouts

Mice that lack the genes for the cytokines tumor necrosis factor (TNF) and interleukin-6 (IL-6) may soon help scientists at the NIEHS sort out the complex roles these molecules play in modulating inflammatory responses to environmental toxins.

Cytokines are released from a wide variety of cell types and regulate neighboring cells. They exhibit diverse and often seemingly unrelated biological effects. For example, cytokines play key roles in development, immunological disorders, infection, and tissue injury.

Dori Germolec, immunotoxicology group leader in the Systems Toxicology Laboratory of the NIEHS, in collaboration with Michael Luster, chief of the Toxicology and Molecular Biology Branch of the National Institute for Occupational Safety and Health, plans to use the knockout mice to study the effects of toxins on cytokine function in the liver, lung, and kidneys. "There are a number of compounds that we have been investigating in our laboratory whose activity is modulated by TNF-alpha," Germolec said. These compounds include dioxin, cadmium, and acetaminophen. The hepatotoxic effects of each of these compounds depend on TNF-α.

"A lot of hepatotoxins are characterized by cellular infiltrations," says Lawrence Schook, chairman of the Department of Veterinary PathoBiology of the University of Minnesota. "TNF, along with IL-1 and IL-6, is associated with inflammation. I think a number of independent observations have shown that TNF is being produced *in situ* for a wide array of hepatotoxins."

Jean Harry, neurotoxicology group leader in the Systems Toxicology Laboratory, of the NIEHS plans to use the cytokine knockout mice to study TNF-α modulation of toxicity of compounds such as triethyl- and trimethyltin in the brain.

TNF-α responses are mediated by two distinct receptor subtypes, TNFR1 and TNFR2. The receptors are expressed in specific tissues. Extracellularly, the two receptors are very similar but intracellularly they have distinct signaling pathways that may account for the different effects of TNF-α in different types of cells. "One cell might have ten times [more] of one receptor than the other," says Schook. "In another cell, it might be the reverse. They both might be

1996 CENR Initiatives

Since its creation in 1993 as part of the National Science and Technology Council, the Committee on Environment and Natural Resources (CENR) has been working to coordinate federal research on environment and natural resources among varying agencies and programs. The CENR has developed its key research initiatives for 1996, which include two new initiatives, three on-going activities at their initial stages of implementation, and two that are in the early stages of discussion.

The CENR is developing a National Ecological Monitoring and Research Program as a new initiative to coordinate current monitoring systems into an integrated, interagency system. Current programs track specific components of the ecosystem but do not provide adequate information on how those components interact. A major goal of the program is to provide insight into how ecosystem health and sustainability are controlled on a regional scale, where policy and management decisions are made.

The second new initiative is the development of a Natural Disaster Information and Mitigation program. In order to reduce the financial burden of natural disasters, which have cost the U.S. economy about $1 billion per week since 1992, the CENR is working on a multi disciplinary research program which will improve national capabilities for risk assessment and risk management. By working with state and local governments to conduct natural hazard risk assessments, the CENR aims to carry out the National Mitigation Strategy, which seeks to cut losses due to natural hazards in half by the year 2020.

The CENR is working to implement the ongoing North American Research Strategy for Tropospheric Ozone (NARSTO) in response to the National Academy of Science's conclusion in 1991 that efforts to control ground-level ozone over the past 20 years had failed, as well as the finding that 53 million people live in areas that exceed the national ambient air quality standard for ozone. This research strategy involves cooperation among the U.S., Canadian, and Mexican governments; industry, and academia.

The CENR is also developing a comprehensive program to study endocrine disrupters, as new information is learned about these chemicals that may cause hormone-related problems such as decreased fertility, cancer, and wildlife population decline. The Endocrine Disrupter Research Strategy will evaluate current data, identify knowledge gaps, and determine what research will be required to fill those gaps.

An international research program to investigate Seasonal to Interannual Climate Change is being funded by the CENR's Global Change Program. This project will examine societal vulnerabilities to climate variation such as floods and droughts, and develop ways to improve scientists' abilities to predict climate changes on a seasonal to interannual time scale.

Finally, activities that the CENR has determined merit additional emphasis but will require more definition to become true initiatives include the proposed Integrated Global Observing System (the CENR plans to develop the U.S. role), and the expansion of economic and social science research to address how human activities affect the environment and how environmental changes impact on society.